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MOLECULAR MODELING IN DESIGN OF FUNCTIONAL NANOSTRUCTURES

MOLEKULÁRNÍ MODELOVÁNÍ V DESIGNU FUNKČNÍCH NANOSTRUKTUR

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Abstract

Molecular modeling using empirical force field represents very efficient tool in structure analysis and in materials design, especially in two cases: (1) The supramolecular system is too large for quantum chemical calculations, (2) The diffraction analysis fails due to the disorder in 3D periodicity of crystal structure. Design of functional nanostructures using molecular modeling in Nanotechnology centre VŠB-TU of Ostrava includes three groups of nanomaterials: (1) functional nanostructures based on the insertion of guest molecules or ions into a suitable inorganic host matrix; (2) nanostructures based on surface modification of suitable host matrix; (3) nanostructures based on self-organization of polar organic molecules.

In all these cases the prediction of structure and properties requires the analysis of the host-guest complementarity, i.e. the mutual relationship between the bonding geometry and charge distribution on the host matrix and guest molecules.

Key words: molecular modeling, functional nanostructures, surface modification

1. Introduction

The main problem in design of supramolecular systems based on the host-guest interaction is the host-guest complementarity, which is characterized by a series of factors describing the presence, ordering and distance of active sites on the host structure, the size of guest molecules, the charge distribution on the host matrix and guest molecules and mutual relation between the host-guest and guest-guest interaction energy. The final supramolecular structure is a result of mutual cooperation of all these factors, which can lead to ordered or partially ordered crystal structure and/or to completely disordered structures [1]. Molecular modeling (i.e.optimization of structure and bonding geometry) using empirical force field can explore the host-guest complementarity and help in prediction of molecular structures and their properties. Empirical force field uses simple analytical expressions to describe individual contributions to bonding energy (bond stretching, bond-angle bending, torsion angle deformations...) and non-bond energy is described by well known expressions describing the electrostatic and van der Waals interactions [2]. This approach enables us to solve the structure of large molecular systems in reasonable time with reasonable accuracy.

It is evident that the description of the total energy of a molecular system by the empirical force field is an approximation which requires extremely careful strategy of modeling, where the experiment must be an integral part of the structure analysis. In the mosaic of experimental methods the X-ray diffraction and infrared spectroscopy play the key roles [3] in the modeling strategy especially in the building of initial models and setting up fixed and variable structure parameters during energy minimization. The modeling strategy based on experimental data has been worked out for organo-inorganic hybrid nanostructures prepared by intercalation and/or surface modification of inorganic layered host structures by various guests (polar organic molecules, organoammonium cations, organic dyes, organometalic complexes, etc.). This strategy includes the force field testing and the systematic generation and automatic sorting of initial models combined with molecular

dynamics in order to find the global energy minimum [4]. The use of this strategy enabled us to solve the surface structures and intercalated layered structures where the diffraction analysis failed due to the lack of perfect three-dimensional structural ordering.

2. Intercalated layered structures

Inorganic layered host structures represents suitable host matrix for insertion (intercalation) of various organic and inorganic guest species. The final product of intercalation is a structure with new properties, which in addition can be tuned by the suitable host-guest combination, by the concentration of guests and by the conditions of preparation (pressure, temperature…).

The most frequently used host matrices are: layer silicates, graphite, tantalum sulfide, vanadyl and zirconium phosphates etc. Organic dyes are very interesting guests, thanks to their optical properties and to a possible tuning these properties by anchoring of dye molecules to a suitable host layer.

An example illustrating the changes of structure and physical properties by intercalation will be given: montmorillonite and vermiculite intercalated with organic dye methylred [5]. Figure 1 a,b shows the interlayer structure of Na-vermiculite (a) and Na- montmorillonite (b) intercalated with methylred. Molecular modeling showed that Na^+ cations in the interlayer space of vermiculite are never fully exchanged by intercalated methylred cations (a) contrary of the interlayer Na^+ cations in montmorillonite, which were entirely replaced by the methylred cations (b).

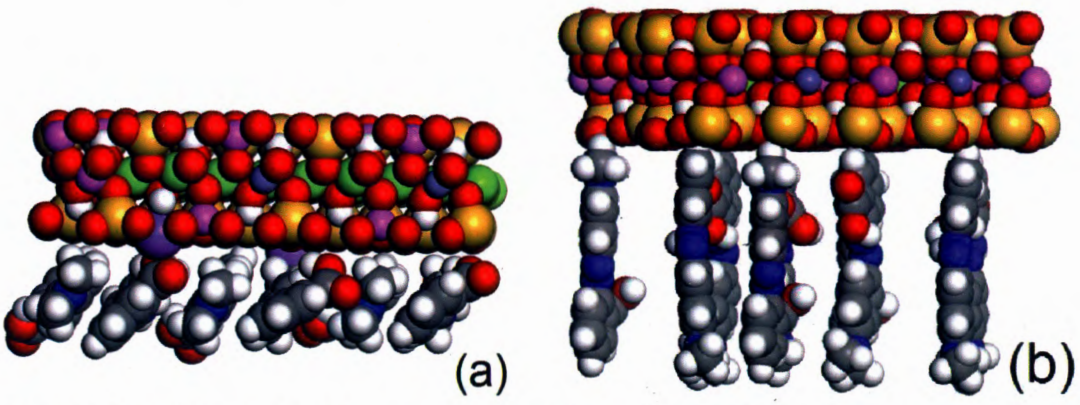

Fig. 1 (a) Optimized model of Na-vermiculite intercalated with methylred. Six methylred cations and two Na^+ cations can be seen in the interlayer. (b) Optimized model of Na-montmorillonite intercalated with five cations and four neutral molecules of methylred

As one can see there is the difference in guest concentration and guest arrangement in the interlayer space of intercalated structure as a result of the different layer charge in the host structure of vermiculite (- 0.80 el per unit cell) and montmorillonite (- 0.50 el per unit cell). Consequently we observed the different shift of photoluminescence band for both intercalates. While the pristine methyl red crystalline powder exhibits the maximum of photoluminescence band at 800 nm, the methyl red vermiculite has band maximum at 645 nm and methyl red montmorillonite at 565 nm.

Furthermore, molecular modeling shed light on the arrangement of molecules in the interlayer space of CdS/vermiculite nanocomposite. CdS/clay nanocomposites are usually synthetized via cation exchange reaction followed by the sulfurization. This process is strongly influenced by the character of the interlayer space, which must be large enough to allow reactants to enter. Atomic force microscopy analysis confirmed that CdS nanoparticles grow mainly on the edges of vermiculite particles out of the interlayer space. CdS molecules are present in the interlayer only in the marginal

part of clay particles and CdS nanoparticles arise on the edges of clay particles. Figure 2 shows optimized model of the vermiculite interlayer near the edge of the clay particle containing water and single CdS molecules. The interlayer space in the middle of clay particles contains H_3O^+ cations and the zone between the middle and marginal part is very disordered as to the composition and arrangement of guests. The calculated interplanar spacing of the basal planes d001 = 1.39 nm and the calculated water content 14.9 wt% is in a very good agreement with X-ray diffraction, infrared spectroscopy and thermogravimetry analysis.

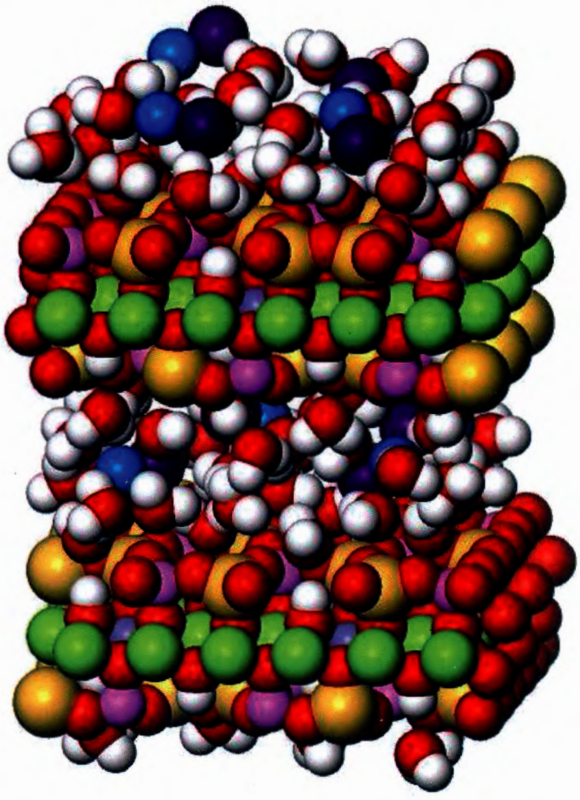

Fig. 2 Optimized model of vermiculite interlayer space. Single CdS molecules (dark violet-blue) surrounded with water molecules can be seen

3. Adhesion of metal nanoparticles on the silicate substrate

Anchoring of various kinds of nanoparticles on the silicate surface is another example how to use layered silicates for the preparation of functional nanostructures. Nanoparticles of metals, metal oxides and metal sulfides anchored on solid substrates offer a wide application field (solar cells, photocatalysts, sensors, antibacterial nanocomposites). In addition, the anchoring eliminates environmental and health risks of the nanoparticles.

Molecular modeling is able to help in preparation of these nanocomposites by the location of adhesion centres, prediction of the sizes of nanoparticles, mutual nanoparticle/substrate crystallographic orientations, etc.

Ag/montmorillonite nanocomposite is an example of nanostructure with antibacterial properties [6]. Figures 3 a,b,c,d show optimized models of Ag nanoparticles with four different sizes

anchored on the Ca-montmorillonite surface. Computed dependence of the total energy on the nanoparticle size enable us to appoint the likeliest size of the single crystalline Ag nanoparticles < 3.3 nm in case that Ag nanoparticles have more than four atomic layers. This result is in good agreement with the high-resolution transmission electron microscopy observations.

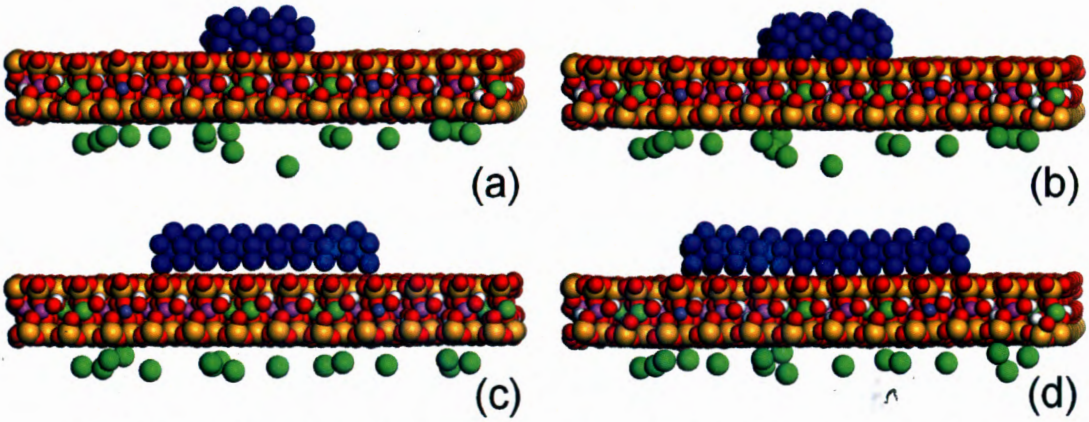

Fig. 3 Optimized models of Ag nanoparticles with our different sizes anchored on the Ca-montmorillonite surface. The Ca2+ cations (green) can be seen under the montmorillonite layer. Energy calculations show that the distinct deformation of nanoparticle structure, which is evident in (a) and (b), is caused by the strong adhesion forces

Molecular modeling also explained the different Ag content observed in various Ag/clay nanocomposites via computation of adhesion energies between the nanoparticle and the substrate. Thus the modeling using the empirical force field was proven to be a useful tool in the investigation of the adhesion and stability of the nanoparticle/clay nanocomposites.

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